

*Citation for published version:*

Torrente-Murciano, L, Villager, T & Chadwick, D 2015, 'Selective oxidation of salicylic alcohol to aldehyde with  $O_2/H_2$  using Au-Pd on titanate nanotubes catalysts', *ChemCatChem*, vol. 7, no. 6, pp. 925-927.  
<https://doi.org/10.1002/cctc.201403040>

*DOI:*

[10.1002/cctc.201403040](https://doi.org/10.1002/cctc.201403040)

*Publication date:*

2015

*Document Version*

Peer reviewed version

[Link to publication](https://doi.org/10.1002/cctc.201403040)

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# Selective oxidation of salicylic alcohol to aldehyde with O<sub>2</sub>/H<sub>2</sub> using Au-Pd on titanate nanotubes catalysts

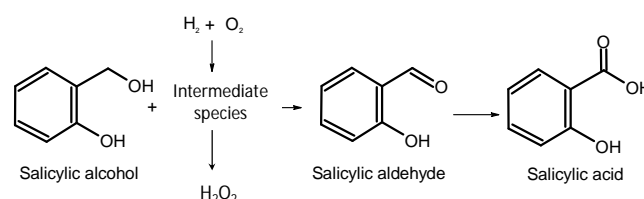
Laura Torrente-Murciano\*<sup>[a,b]</sup>, Thomas Villager<sup>[b]</sup> and David Chadwick\*<sup>[a]</sup>

**Abstract:** Alcohol oxidation with 100% selectivity to the aldehyde product (versus acid formation) is achieved at mild conditions by a tandem-type system where the intermediate species of hydrogen peroxide formation from an O<sub>2</sub>/H<sub>2</sub> mixture are formed and utilised directly over Au-Pd/Ti-NT catalysts. In-situ reaction of the intermediate species minimises the parallel decomposition of hydrogen peroxide into water, overcoming one of the limitations on the use of hydrogen peroxide as a green oxidant.

There is a current significant scientific effort concerning the development of cleaner catalytic selective oxidation processes using hydrogen peroxide<sup>[1]</sup>, molecular oxygen<sup>[2]</sup> and compressed air<sup>[3]</sup> to substitute stoichiometric oxidants at industrial scale. In particular, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is an oxidizing agent with a high active oxygen content that produces only water as a co-product. However, the large scale use of H<sub>2</sub>O<sub>2</sub> still presents a series of challenges associated with waste production from its anthraquinone autoxidation synthesis and safe transport and storage. Consequently, there has been a continuing interest in the local direct synthesis of hydrogen peroxide from H<sub>2</sub> and O<sub>2</sub><sup>[4]</sup>. We have recently reported the high activity of Au-Pd nanoparticles supported on titanate nanotubes (Ti-NT) for the direct synthesis of H<sub>2</sub>O<sub>2</sub> with productivities in excess of 10 kmol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>metal</sub><sup>-1</sup> h<sup>-1</sup>. The high activity of these nanostructured catalysts is due to a very small metal particle size (<1.5 nm) and high dispersion afforded by its high metal-support interaction and physical constraints created by the high aspect ratio morphology of the support<sup>[5]</sup>. Despite the potential of this catalytic system, the hydrogen utilization is compromised by the parallel decomposition of H<sub>2</sub>O<sub>2</sub> to water and oxygen. To avoid this problem, integration of the *in-situ* generation and utilization of hydrogen peroxide is presented as an efficient way of reducing cost, avoid intermediate purification or separation steps, and transportation and storage of H<sub>2</sub>O<sub>2</sub><sup>[6]</sup>. Ultimate integration would be achieved by aligning the rate of H<sub>2</sub>O<sub>2</sub> production and consumption, ideally with the use of only a single catalyst for both reaction steps.

The current development of gold-based catalysts for oxidation reactions<sup>[7]</sup> and reported outstanding selectivities<sup>[7b, 8]</sup> has prompted the use of Au-Pd on titanate nanotubes catalyst for the tandem generation of H<sub>2</sub>O<sub>2</sub> and in situ oxidation reactions.

An interesting oxidation reaction is the selective oxidation of o-hydroxy benzylalcohol (salicylic alcohol) to o-hydroxy benzaldehyde (salicylic aldehyde), which is an intermediate compound for the synthesis of pesticides, polymers, perfumes, etc<sup>[9]</sup>, serving as a model reaction for selective oxidation in aqueous phase. Several patents have covered this reaction<sup>[10]</sup> based on processes using palladium and platinum catalysts and promoters (bismuth, lead, tellurium, etc.). The current main limitation is the formation of by-products which are difficult to eliminate from the aldehyde product, requiring several additional separation steps. In this paper, we demonstrate tandem generation and utilization of oxidation species from a mixture of H<sub>2</sub> and O<sub>2</sub> in the selective oxidation of salicyl alcohol to aldehyde without the formation of acid as depicted in Figure 1.



**Scheme 1.** Tandem generation and utilization of oxidising species in selective oxidation of salicylic alcohol.

Gold-palladium nanoparticles supported on titanate nanotubes present a 100% selectivity in the oxidation of salicylic alcohol to its corresponding aldehyde using a mixture of O<sub>2</sub>/H<sub>2</sub>, with no acid formation. This bi-metallic system provides comparable activity to its equivalent Pd-only/Ti-NT catalyst and the same exceptional selectivity towards the aldehyde product as achieved with the Au-only catalyst supported on Ti-NT (Table 1). This synergetic effect of Au-Pd bimetallic particles is in agreement with previous observations in the literature<sup>[11]</sup>.

The high aldehyde productivity (198.0 mol aldehyde kg<sub>metal</sub><sup>-1</sup> h<sup>-1</sup>) of the Au-Pd/Ti-NT catalyst is related to the small metal particle size recently determined using high angle annular dark field (HAADF) images taken in an aberration corrected STEM<sup>[5]</sup> and the unique metal-support interaction. Although the majority of the metal forms particles with a mean value of 1.5 nm (standard deviation 0.5 nm), single atoms decorating the support are also present. These small particle sizes are in agreement with the lack of gold and palladium diffraction peaks in the X-ray diffraction (XRD) pattern, where only the peaks corresponding to the Ti-NT support are observed. Energy dispersive X-ray spectroscopy (STEM-XEDS) confirmed that the supported particles were Au-Pd alloys, where the larger particles are usually Au-rich while the very small clusters are Pd-rich<sup>[5]</sup>.

The selectivity of gold-palladium particles supported on Ti-NT was compared with Au-Pd catalysts using commercial ceramic oxide supports (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) under the same

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reaction conditions, Table 1. All these catalysts have been shown to be active for the direct synthesis of  $\text{H}_2\text{O}_2$  [5] and present a comparable oxidation activity than the Au-Pd/Ti-NT in the tandem system. It is important to note that the catalysts supported on commercial oxides are not optimized systems which likely present a broad particle size distribution, where only small metal particles (<5 nm) are responsible of their activity [12]. Despite this, an outstanding selectivity to the aldehyde (intermediate oxidation product) is observed for the Au-Pd/Ti-NT, with no measurable acid formation compared to the other Au-Pd catalysts supported on commercial oxides. The high aldehyde yield of the Au-Pd/Ti-NT is related to the unique metal – support interaction achieved during the synthesis of the Au-Pd/Ti-NT catalyst where metal cations are exchanged by protons at the surface of the Ti-NT support [13].

**Table 1.** Oxidation of salicylic alcohol with a mixture of  $\text{H}_2/\text{O}_2$ : effect of catalytic support

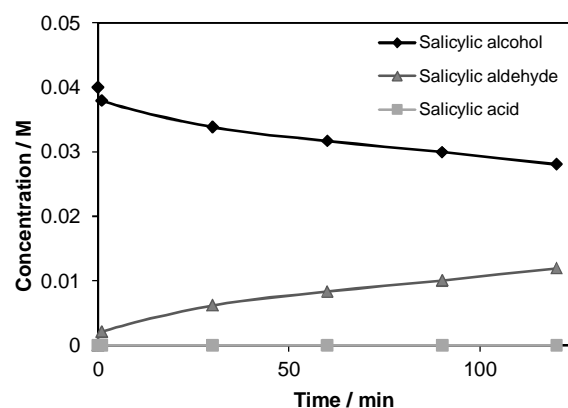
Support	Au content / wt. %	Pd content / wt. % [b]	Conversion / %	Aldehyde selectivity / %	Productivity <sup>[a]</sup> / mol <sub>ald</sub> kg <sub>met</sub> <sup>-1</sup> h <sup>-1</sup>
Ti-NT	0.4	1.1	29.7	100	198.0
Ti-NT	1.5	-	3.0	100	20.0
Ti-NT	-	1.5	33.3	91.9	204.0
SiO <sub>2</sub>	1.5	1.5	34.0	53.6	121.5
Al <sub>2</sub> O <sub>3</sub>	1.5	1.5	18.8	94.5	118.4
TiO <sub>2</sub>	1.5	1.5	13.2	42.2	37.1

Reaction conditions: 0.04M salicylic alcohol, 75 mL methanol, catalysts: 150 mg reduced under  $\text{H}_2$  at 200 °C, 0.04 M NaCl, 20 bar ( $\text{O}_2/\text{H}_2/\text{N}_2$ :5/5/90 5), 50 °C, 2 h [a] Productivity: mol salicylic aldehyde kg<sub>metal</sub><sup>-1</sup> h<sup>-1</sup>

The reaction profile for the oxidation of salicylic alcohol using the Au-Pd/Ti-NT catalyst during the tandem system (Figure 1) fits well with a first order reaction with respect to the alcohol concentration during the first hour of the reaction after which, a rate decrease is observed due to a combination of factors. On one hand, we have previously shown that the synthesis of hydroperoxy species (and hydrogen peroxide) peaks at 50 minutes of reaction after which, the decomposition rate is higher than the synthesis rate, with both reactions competing for the active sites. Additionally, the rate of formation of hydroperoxy species is expected to decrease as the oxygen and hydrogen partial pressure decreases in the gas phase, consequently having a detrimental effect on the oxidation rate (reaction in series). No metal leaching was observed. Similar reaction profiles are observed for the other Au-Pd systems.

To further understand the tandem oxidation system, the oxidation activity of the Au-Pd/Ti-NT catalyst was compared using added hydrogen peroxide, oxygen and an  $\text{O}_2/\text{H}_2$  mixture (Table 2). Very low conversion (and high selectivity) was

achieved when oxygen ( $P_{\text{O}_2} = 2$  bar) is used as oxidant. The turnover frequency values (TOF) were aligned with those



**Figure 1.** Reaction profile of the oxidation of salicylic alcohol with a mixture of  $\text{H}_2/\text{O}_2$  using Au-Pd/Ti-NT catalyst.

reported in the literature for similar salicylic alcohol oxidation systems [9]. Negligible conversion to oxidation products was observed when hydrogen peroxide is added as the oxidant under a nitrogen atmosphere.  $\text{H}_2\text{O}_2$  decomposes on the surface of the Au-Pd/Ti-NT ( $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \frac{1}{2} \text{O}_2$ ) with a reported pseudo-first order rate constant of  $0.049 \text{ min}^{-1}$  [5]. During the reaction, evolution of oxygen bubbles on the catalyst surface was observed due to  $\text{H}_2\text{O}_2$  decomposition, which probably significantly limits the access of the salicylic alcohol reactant to the catalyst surface. These observations demonstrate that in the tandem system using an  $\text{O}_2/\text{H}_2$  mixture, neither *in-situ* formed hydrogen peroxide nor the oxygen in the gas phase are directly responsible of the oxidation of the alcohol. Alternatively, it is suggested that *in-situ* generated intermediate species on the surface of the Au-Pd/Ti-NT catalysts involved in  $\text{H}_2\text{O}_2$  formation are responsible for the tandem oxidation of salicylic alcohol. These species are *in-situ* consumed by the oxidation reaction before  $\text{H}_2\text{O}_2$  is released or decomposed. It can be speculated that hydroperoxy species are the intermediate involved [14].

**Table 2.** Oxidation of salicylic alcohol: effect of oxidant

Catalyst	Oxidant	Conversion / %	Aldehyde selectivity / %	Productivity <sup>[a]</sup> / mol <sub>ald</sub> kg <sub>met</sub> <sup>-1</sup> h <sup>-1</sup>
Au-Pd/Ti-NT	$\text{H}_2\text{O}_2(\text{N}_2)$ <sup>[b]</sup>	< 1	-	-
Au-Pd/Ti-NT	$\text{H}_2\text{O}_2(\text{N}_2)$ <sup>[c]</sup>	<1	-	-
Au-Pd/Ti-NT	$\text{O}_2$ (10%)	2.2	100	14.7
Au-Pd/Ti-NT	$\text{H}_2/\text{O}_2$ (5%/5%)	29.7	100	198.0

Reaction conditions: 0.04M salicylic alcohol, 75 mL methanol, catalysts: 150 mg reduced under  $\text{H}_2$  at 200 °C, 0.04 M NaCl, 20 bar ( $\text{O}_2/\text{H}_2/\text{N}_2$ :5/5/90 5), 50 °C, 2 h [a] Productivity: mol salicylic aldehyde kg<sub>metal</sub><sup>-1</sup> h<sup>-1</sup>, [b] [ $\text{H}_2\text{O}_2$ ] = 0.2 M, [c] [ $\text{H}_2\text{O}_2$ ] = 0.035 M

The tandem system presented here can proceed without the addition of base, which is usually considered to be essential to facilitate the desorption of the products from the catalyst surface [7b]. 100% selectivity and similar activities are observed with the addition of NaCl, NaOH or Na<sub>2</sub>CO<sub>3</sub> to the reaction medium (Table 3). Interestingly, the presence of a halide (NaCl) did not have any significant effect with respect to other additives NaOH and Na<sub>2</sub>CO<sub>3</sub> although the former is known to stabilise hydrogen peroxide and lower its decomposition [15], while the latter favours its rapid decomposition. Indeed, the absence of additives also presented similar conversion and selectivity values, probably due to the Na and/or OH traces remaining on the support after the nanotubes synthesis. This lack of additive effect supports the view that formed H<sub>2</sub>O<sub>2</sub> is not the oxidising species in the tandem system but the intermediate hydroperoxy species.

**Table 3.** Oxidation of salicylic alcohol with in-situ synthesised species: effect of additive nature.

Catalyst	Additives	Conversion / %	Aldehyde selectivity / %	Productivity <sup>[a]</sup> / mol <sub>ald</sub> kg <sub>met</sub> <sup>-1</sup> h <sup>-1</sup>
Au-Pd/Ti-NT	NaCl	29.7	100	198.0
Au-Pd/Ti-NT	NaOH	31.9	100	212.5
Au-Pd/Ti-NT	Na <sub>2</sub> CO <sub>3</sub>	27.2	100	181.3

Reaction conditions: 0.04M salicylic alcohol, 75 mL methanol, catalysts: 150 mg reduced under H<sub>2</sub> at 200 °C, 0.04 M additive, 20 bar (O<sub>2</sub>/H<sub>2</sub>/N<sub>2</sub>:5/5/90.5), 50 °C, 2 h [a] Productivity: mol salicylic aldehyde kg<sub>metal</sub><sup>-1</sup> h<sup>-1</sup>

In conclusion, in-situ formation and utilization of intermediate oxidising species from O<sub>2</sub>/H<sub>2</sub> mixtures in a tandem-type system minimises the parallel decomposition of hydrogen peroxide and maximises hydrogen utilization. The Au-Pd/Ti-NT catalyst achieves 100% selectivity towards aldehyde formation with higher productivities than equivalent catalysts supported on conventional oxides. Intermediate species involved in the direct synthesis of hydrogen peroxide are believed to be the oxidizing species formed on the metal surface of the Au-Pd/Ti-NT catalyst but further investigations are required to identify them.

## Experimental Section

Titanate nanotubes were synthesised by a hydrothermal method previously described in detail [16]. Gold and palladium was simultaneously loaded on the Ti-NT by adsorption [13b] using gold chloride (HAuCl<sub>4</sub>) and palladium chloride (PdCl<sub>2</sub>) as precursors. The final metal loading was determined by dissolving the catalysts with a mixture 1:3 of HNO<sub>3</sub>:HCl, analysed by inductively coupled plasma (ICP, PE Optima 2000 DV). Au-Pd catalysts over conventional supports such as SiO<sub>2</sub> (EP-10, Crosfield Chemicals), Al<sub>2</sub>O<sub>3</sub> (activated, 50-200 microns, Acros Organics) and TiO<sub>2</sub> (anatase nanopowder, Sigma Aldrich) were prepared by wetness impregnation followed by calcination at 400 °C. All catalysts were reduced under H<sub>2</sub> flow at 200 °C during 90 minutes.

Catalyst activity studies were carried out in a Parr stainless steel autoclave reactor (250 mL) equipped with glass liner. Reaction temperature was controlled externally by a mantle heater. A four propeller gas aspirating stirrer was used for agitation at a speed of 1000 rpm. In a typical experiment, 0.15 g of catalyst are loaded in 75 mL of methanol containing 372.4 mg of salicylic alcohol (0.04 M) and 0.04 M of the selected additive (NaOH, NaCO<sub>3</sub> or NaCl) if used. The reactor was then purged with hydrogen three times. Once the temperature was stable at 50 °C, the autoclave was filled with a mixture of H<sub>2</sub>/O<sub>2</sub>/Ar (5/5/90 %) at 20 bar of pressure. Liquid samples were taken at regular intervals and analysed by HPLC (Perkin Elmer Series 200) equipped with a UV detector. The mass balance was satisfied within 10% error.

## Acknowledgements

The authors would like to thank Prof Christopher Kiely and Dr Qian He for their supportive catalyst characterization work using STEM-HAADF.

**Keywords:** hydrogen peroxide • gold • palladium • selective oxidation • tandem reactions

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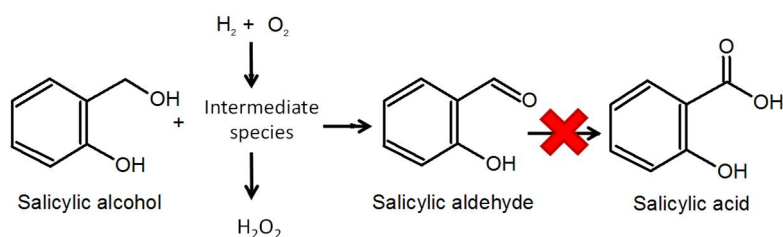
## Entry for the Table of Contents

## COMMUNICATION

L. Torrente-Murciano\*, T. Villager and D. Chadwick

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**Selective oxidation of salicylic alcohol to aldehyde with O<sub>2</sub>/H<sub>2</sub> using Au-Pd on titanate nanotubes catalysts**



In-situ formation and utilization of intermediate oxidising species from O<sub>2</sub>/H<sub>2</sub> mixtures in a tandem-type system minimises the parallel decomposition of hydrogen peroxide with 100% selectivity to the aldehyde product.